

# Forces and conformation of a polyelectrolyte chain between two charged walls

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We investigate forces between two charged macroscopic surfaces where the intervening medium is composed of a uni-univalent electrolyte plus an additional, infinitely long polyelectrolyte chain. The level of the theory is the same as the usual Poisson-Boltzmann scheme, upgraded by a self-consistent inclusion of the polyelectrolyte configurational statistics into the statistical sum. The equations obtained are solved analytically in the limit of small polymer charge and small intersurface separation as compared with the Debye screening length. The interaction free energy as a function of separation between the surfaces behaves in a markedly different way compared to the case of no intervening polyelectrolyte. The surprising feature of the force characteristics is an additional attractive force derivable even in the mean-field approximation.

## 1. Introduction

The problem of interaction between charged macroscopic surfaces immersed in an electrolyte solution has received much attention through years [1] and has been recently worked out on an accuracy level equal to the one achieved by the bulk liquid state theories [2]. The most important recent advance in the field is the demonstration that the usual mean-field (Poisson-Boltzmann) theory in certain physically realistic cases does not predict correctly even the sign of the interaction, i.e. forces between equally charged surfaces can become attractive [2,3]. This effect is due to the fluctuations in the local distribution of ions close to the surfaces and is therefore completely missed by the mean-field (PB) approach.

If this problem has been well worked out, an upgraded version of it, where the intervening medium contains charged polymers as well as charged ions is only beginning to be scrutinized by an appropriate theoretical approach [4].

Though the polyelectrolyte theory has a long standing with many significant results [5], the problem of confined polyelectrolytes interacting with charged surfaces is still in its infancy. In this context we should especially mention the seminal work of Wiegel [6], who treated the conformational prop-

erties of a polyelectrolyte chain interacting with a single surface. He showed that by changing the charge density residing on the surfaces a phase transition between surface-bound and extended configurations of the polyelectrolyte chain can be accomplished. More recently Miklavic and Marčelja [7] have treated the interaction between charged walls carrying grafted polyelectrolytes and immersed in an electrolyte solution, basing their analysis on the self-consistent field method devised for neutral polymers by Milner, Witten and Cates [8]. They analysed the modifications in the interaction pressure brought about by the presence of polyelectrolyte chains. A further step in the understanding of interactions between charged surfaces with intervening polyelectrolyte chains has been accomplished by Åkesson, Woodward and Jönsson, in a combined Monte Carlo-analytical (Poisson-Boltzmann) approach [4]. Their model system was composed of two charged surfaces with oppositely charged polyelectrolyte chains in between. They showed that the connectivity of the polyelectrolyte chains can be the cause of pronounced attractive interactions due to the bridging of the chains from one surface to the other one. This is indeed surprising since on the Poisson-Boltzmann level, without any connectivity between the charged species – that is to say, the forces be-

tween equally charged surfaces are always repulsive.

In this contribution we shall go one step further and treat a model system composed of two charged surfaces immersed in a uni-univalent electrolyte plus a single polyelectrolyte chain of infinite extent. Our method of solving the problem will be very close to the recently introduced functional-integral approach to the confined Coulomb fluids [9]. Since we showed that the Poisson-Boltzmann description of a simple Coulomb fluid can be obtained from the saddle-point configuration of an appropriate field theory, we shall try to proceed likewise in this more complex situation. We shall derive a coupled set of two equations, one describing the electrostatic field configuration and the other one the polymer segment density distribution, that supersede the single PB equation valid for the case with no polyelectrolyte present. A limiting case where a simple analytical solution is feasible will be discussed in detail.

2. Theory

Our model system will be composed of a uni-univalent electrolyte of ionic charge  $e_0$  and dielectric constant  $\epsilon$  in equilibrium with a bulk reservoir of absolute activity  $z_0$ , plus a polyelectrolyte chain of charge  $\tau$  per bead of extension  $l$  with a total contour length  $Nl$ , both confined between two electrified surfaces, separated by  $2a$  and each carrying a surface charge density  $\sigma$ , fig. 1. The surfaces are supposed to be impenetrable for ions as well as the polyelectrolyte. For such a system the configurational part of the Hamiltonian can be written in a discretized form

$$H = \frac{3kT}{2l^2} \sum_p (r_{p+1} - r_p)^2 + \frac{1}{2} \sum_{i,j} e_i e_j u(r_i, r_j) - \frac{1}{2} \sum_k N_k e_k^2 u(r, r') + \sum_i e_i \phi_e(r_i), \tag{1}$$

where  $u(r, r') = 1/4\pi\epsilon\epsilon_0|\mathbf{r}-\mathbf{r}'|$  is the bare Coulomb potential between two unit charges located at  $\mathbf{r}$  and  $\mathbf{r}'$ , while  $kT$  is the thermal energy. In the above equation index  $p$  runs over all the polymer beads. Indices  $i$  and  $j$  run over all the polymer beads ( $e_i = \tau$ ), all anions ( $e_i = -e_0$ ) and all cations ( $e_i = e_0$ ) while index  $k$  can designate the polymer ( $N_k e_k^2 = N\tau^2$ ), the cations ( $N_k e_k^2 = N_e e_0^2$ ) or the anions ( $N_k e_k^2 = N_a e_0^2$ ).

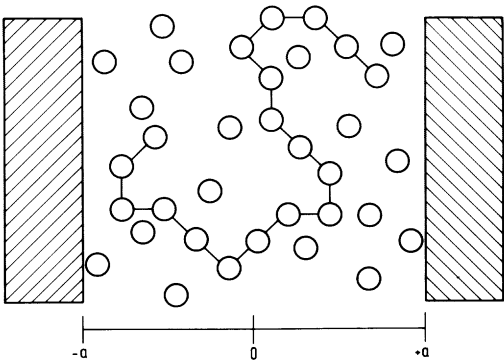


Fig. 1. The model system. Two charged surfaces (surface charge density  $\sigma$ ) at a separation  $2a$  with a uni-univalent electrolyte plus an infinitely long polyelectrolyte chain (charge per bead  $\tau$ ) in between. The dielectric constant  $\epsilon$  is supposed to be the same in all regions of the space. Surfaces are impenetrable to ions as well as to the polyelectrolyte. Ions are allowed to exchange with the bulk reservoir.

$\phi_e(\mathbf{r})$  is the external electrostatic potential due to the charges on the surfaces. In what follows we shall strictly use a continuum representation of the Gaussian chain that amounts to the following formal replacement

$$\sum_p (r_{p+1} - r_p)^2 \rightarrow \int_0^N \left( \frac{d\mathbf{R}(n)}{dn} \right)^2 dn,$$

where  $\mathbf{R}(n)$  now stands for the coordinate of the  $n$ th bead along the polymeric chain.

We now construct the partition function for the system characterized by the configurational Hamiltonian  $H$ . Since we allow for the exchange of the ions with the bulk reservoir the appropriate form of the partition function should be used

$$\Xi = \prod_a \sum_{N_a=0}^{\infty} \frac{\zeta^{N_a}}{N_a!} \int_{[\mathbf{R}, \mathbf{r}]} \exp(-\beta H) \mathcal{D}\mathbf{R}(n) \mathcal{D}^{N_a} \mathbf{r}, \tag{2}$$

where  $\mathcal{D}f = \lim_{n \rightarrow \infty} df_1 df_2 \dots df_n$ ,  $a$  is the index of ionic species,  $a$ =cations, anions,  $\zeta$  is the renormalized value of the absolute activity,  $\zeta = z_0 \times \exp(\frac{1}{2}\beta e_0^2 u(r, r'))$  and  $\beta$  is the inverse thermal energy,  $\beta^{-1} = kT$ .

We now proceed in the same way as we did in the case where no polyelectrolyte is present, that is, we introduce the Hubbard-Stratonovich transforma-

tion for all the pair potentials, reducing them to effective single particle interactions with the auxiliary field, that is closely linked with the local electrostatic potential [9]. We shall relegate all the nasty details of the formal manipulations to a later publication [10] and quote here only the final results. First of all the partition function, eq. (2), can be thus transformed into a compact form

$$\Xi = \Delta(\beta) \exp[\beta U_p(N)]$$

$$\times \int \int \langle G_\phi(\mathbf{R}, \mathbf{R}'; N) \rangle_\phi d^3\mathbf{R} d^3\mathbf{R}', \quad (3)$$

where  $\Delta(\beta) = (2\pi)^{N/2} [\det \beta u^{-1}(\mathbf{r}, \mathbf{r}')]^{1/2}$  and  $U_p(N)$  is the electrostatic self-energy of the polyelectrolyte chain.  $G_\phi(\mathbf{R}, \mathbf{R}'; N)$  in the above equation is the conditional probability (Green's function) that a polyelectrolyte chain  $N$  segments long will reach point  $\mathbf{R}$  after starting from point  $\mathbf{R}'$  while moving in an external potential equal to  $(\beta\tau)\phi(\mathbf{r})$  [11]. The  $\phi$  average stands for the following operation

$$\langle \rangle_\phi = \int_{[\phi]} \dots \exp[-\beta F_{PB}(ie_0)] \mathcal{D}\phi(\mathbf{r}), \quad (4)$$

where  $F_{PB}(ie_0)$  has already been encountered while evaluating the grand canonical partition function of an inhomogeneous electrolyte [9]; it is nothing but the Poisson–Boltzmann free energy

$$F_{PB}(e_0) = -\frac{1}{2} \epsilon \epsilon_0 \int [\nabla \phi(\mathbf{r})]^2 d^3\mathbf{r} - 2kT\zeta \int \cosh[\beta e_0 \phi(\mathbf{r})] d^3\mathbf{r} - \oint \phi(\mathbf{r}) \sigma d^2\mathbf{r} \quad (5)$$

evaluated at imaginary values of the charges. This is not too strange since in the saddle-point approximation, which is our next step, all the local potentials are purely imaginary and lead to a PB equation with a real potential.

We now perform the saddle-point approximation [12] on the  $\phi$  average in eq. (3). This should lead us to the PB theory in the case if no polyelectrolyte is present. We therefore expect that the saddle-point equations derived from eq. (3) will give us the most immediate generalization of the PB theory in the presence of an additional polyelectrolyte chain. These equations turn out to have the following coupled form

$$\epsilon \epsilon_0 \nabla^2 \phi = 2\zeta e_0 \sinh(\beta e_0 \phi) - \tau \rho_\phi, \quad (6)$$

$$\left( \frac{\partial}{\partial N} - \frac{l^2}{6} \nabla^2 + \beta \tau \phi \right) G_\phi(\mathbf{R}, \mathbf{R}'; N) = \delta^3(\mathbf{R} - \mathbf{R}') \delta(N), \quad (7)$$

where the coupling is provided through the  $\phi$  dependence of the polyelectrolyte segment density  $\rho_\phi(\mathbf{r})$  that can also be written by way of solution of eq. (7) as [13]

$$\rho_\phi(\mathbf{r}) = \frac{\int \int d^3\mathbf{R} d^3\mathbf{R}' \int_0^N dn G_\phi(\mathbf{R}, \mathbf{r}; N-n) G_\phi(\mathbf{r}, \mathbf{R}'; n)}{\int \int d^3\mathbf{R} d^3\mathbf{R}' G_\phi(\mathbf{R}, \mathbf{R}'; N)}. \quad (8)$$

Also, the saddle-point configuration satisfies the usual electroneutrality condition in the form

$$\epsilon \epsilon_0 \frac{\partial \phi}{\partial \mathbf{n}} = -\sigma, \quad (9)$$

where  $\mathbf{n}$  is the local normal of the bounding surfaces situated at  $z = \pm a$ . Eqs. (6) through (9) represent the proper generalization of the PB equation in the presence of a single polyelectrolyte chain. Their solution gives the self-consistent form of the electrostatic potential in the region between the two surfaces. In order to avoid confusion we shall refer to eqs. (6)–(9) as the single-chain Poisson–Boltzmann theory for polyelectrolytes (SC-PBP).

The major difference between our work and the approximation scheme devised by Åkesson, Woodward and Jönsson (PPB approximation) [4], leaving aside the presence of additional electrolyte, is in the fact that the statistical average over polyelectrolyte configurations is done explicitly in our case, leading to eqs. (7) and (8), while it is done numerically in their case.

### 3. An approximate solution of the basic equations

The above set of SC-PBP equations presents two coupled non-linear differential equations with no immediate general solution in sight. They belong to the general class of results derivable through the self-consistent field method [14] standardly used in the context of polymer excluded volume interactions.

The main complication with regard to this case is that the self-consistent field is not simply a linear function of  $\rho_\phi(\mathbf{r})$  but is instead given as a solution of eq. (6).

Instead of turning immediately to numerical manipulation of the basic equations, we shall first of all construct an approximate analytical solution valid under certain restrictive conditions to be explained in what follows.

Our starting point is the thermodynamic limit  $N \rightarrow \infty$ ,  $S \rightarrow \infty$  (in this particular order) with finite  $N/S$ , where  $S$  is the surface area of the bounding surfaces. This limit invariably leads to the ground-state dominance ansatz [13] for the polymer Green's function  $G_\phi(\mathbf{R}, \mathbf{R}'; N)$  and in addition to the conclusion that the system has to be homogeneous in the transverse ( $x, y$ ) directions. Furthermore we shall linearize eq. (6) in  $\phi$ , that subsequently leads to an inhomogeneous Debye-Hückel equation, with a source term equal to  $-\tau\rho_\phi(\mathbf{r})$ . Its solution satisfying the boundary condition, eq. (9), can now be written down explicitly as

$$\phi(z) = -\frac{\tau}{\epsilon\epsilon_0} \int_{-a}^a g_\kappa(z, z') \rho_\phi(z') dz' - \frac{\sigma}{\epsilon\epsilon_0 \kappa} \frac{\cosh(\kappa z)}{\sinh(\kappa a)}, \quad (10)$$

where  $g_\kappa(z, z')$  is an appropriate Green's function of the Debye-Hückel equation and  $\kappa$  is the standard inverse Debye screening length. However, even this linearization ansatz is not enough to obtain an explicit polymer Green's function, i.e. a solution of eq. (7). This is due to the fact that the first term in the linearized solution, eq. (10), still contains  $\rho_\phi$ . We shall consequently introduce another approximation, first used in a similar context by Wiegel [6], that imposes a restriction on the magnitude of  $\tau$  of the form  $\tau \ll \sigma l^2$  and essentially guarantees that the electrostatic interactions between the beads on the polyelectrolyte chain (the first term in eq. (10)) can be neglected in comparison with the direct interactions of the beads with the charges on the surfaces (the second term in eq. (10)).

Finally we shall also restrict ourselves to the case of  $\kappa a \ll 1$ , but solely to give the mathematics a more transparent form. A general solution without this last restriction is possible but, unfortunately, the ensuing

mathematical technicalities connected with the solutions of the modified Mathieu equation tend to completely overrun the underlying physics [10].

After acknowledging the relevant approximations that we made, we can now state the final form of the SC-PBP equations that will be the starting point of our subsequent discussion. First of all the longitudinal part of the Green's function can be written in the standard ground-state dominance form [13]

$$G_\phi(z, z'; N) = \psi(z) \psi(z') \exp(-E_N N), \quad (11)$$

where  $\psi(z)$  is a solution of

$$\frac{d^2\psi(z)}{dz^2} + \kappa^2 \{ \epsilon_N + \theta(a) [1 + \frac{1}{2}(\kappa z)^2] \} \psi(z) = 0, \quad (12)$$

with

$$\theta(a) = \frac{6\beta\tau\sigma}{\epsilon\epsilon_0 \kappa (\kappa l)^2} \operatorname{csch}(\kappa a) \quad \text{and} \quad \epsilon_N = \frac{6E_N}{(\kappa l)^2}. \quad (13)$$

Furthermore since  $G_\phi(z, z'; N)$  has to be an even function of both its spatial arguments and has to vanish at the impenetrable walls,  $\psi(z)$  has to satisfy two additional boundary conditions, i.e.

$$\frac{d\psi(z)}{dz} (z=0) = 0 \quad \text{and} \quad \psi(z=\pm a) = 0. \quad (14)$$

We have therefore reduced our basic equations to an eigenvalue problem, eq. (12), where special care has to be taken to obtain the lowest lying energy eigenvalue if  $\epsilon_N > 0$  and, conversely, the highest lying eigenvalue if  $\epsilon_N < 0$ , see ref. [6] for details.

#### 4. Results

The basic equation that we have to solve, eq. (12) of section 3, looks like a harmonic oscillator equation with a reversed potential, which, with the proper choice of dimensionless variables, can be reduced to a parabolic cylinder equation [15]. Introducing the following two dimensionless variables

$$\xi^2 = \sqrt{2\theta(a)} (\kappa z)^2 \quad \text{and} \quad \alpha = -\frac{\epsilon_N + \theta(a)}{\sqrt{2\theta(a)}}, \quad (15)$$

we can write the unnormalized solution of eq. (12) that displays an even symmetry as

$\psi(z) \sim W(\alpha, \xi) + W(\alpha, -\xi) \, , \tag{16}$

where  $W(x, y)$  is the appropriate parabolic cylinder function [15]. The second boundary condition, eq. (14), now reads

$\psi(a) = \psi(\xi_0) = 0 \quad \text{with} \quad \xi_0^2 = \sqrt{2\theta(a)} (\kappa a)^2 \, , \tag{17}$

giving us  $\alpha = \alpha(\xi_0)$ , wherefrom through eq. (15) we obtain  $\epsilon_N = \epsilon_N(a)$ . In the case of ground-state dominance, eq. (11), the saddle-point free energy is obtained from eq. (3) as

$$F = -kT \ln \Xi = kTE_N N + F_{PB}$$
$$= kT \frac{(\kappa l)^2}{6} \epsilon_N(a) N + F_{PB} \, , \tag{18}$$

where  $F_{PB}$  is the standard linearized Poisson–Boltzmann free energy for constant surface charge density [1]. In what follows we shall confine ourselves to the analysis of the first term in eq. (18) that is the only one specific for the confined polyelectrolyte problem.

Numerical investigation of the boundary condition, eq. (17), see fig. 2, now leads to the conclusion that for  $\xi_0 \ll 1$  we have  $\alpha \ll -1$ . In the opposite limit  $\xi_0 \gg 1$  we have  $\alpha \gg 1$ . This allows us to use certain asymptotic expressions valid for solution, eq. (16), in different regimes of  $\alpha$  values [15]. First of all for  $\alpha \ll -1$  we end up with

$\psi(\xi_0) \sim \sqrt{2} W(\alpha, 0)$ 
$$\times [\cos(\sqrt{-\alpha} \xi_0 + \pi/4) + \sin(\sqrt{-\alpha} \xi_0 + \pi/4)] \, , \tag{19}$$

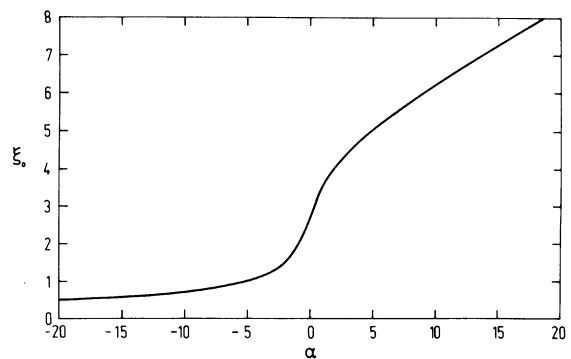


Fig. 2. Numerical solution of the boundary condition, eq. (17), giving the  $\alpha = \alpha(\xi_0)$  dependence in the range of  $\xi_0$  values where the asymptotic analysis of eqs. (19) and (21) is not accurate.

wherefrom the boundary condition, eq. (17), leads to  $\sqrt{-\alpha} \xi_0 = -\pi/2$ . This can be converted into an appropriate form for  $\epsilon_N(a)$  leaving us with

$\epsilon_N(a) \approx \left(\frac{\pi}{2}\right)^2 \frac{1}{(\kappa a)^2} - \theta(a) \, , \quad \text{when} \quad \xi_0 \ll 1 \, . \tag{20}$

The first term in the above equation is apparently nothing but the steric interaction between two surfaces with a polymeric chain in between, derived first by Edwards and Dolan [16]. As the intersurface separation gets small enough the electrostatic effects are completely lost and we remain with an essentially “discharged” system where all the relevant interactions are due to steric confinement.

In the opposite limit of  $\alpha \gg 1$  we can find the following asymptotic representation of the solution, eq. (16):

$\psi(\xi_0) \sim \sqrt{2\pi} \alpha^{-1/12} \exp(\tfrac{1}{2}\pi\alpha) \text{Ai}\left(\frac{\alpha - \frac{1}{4}\xi_0^2}{\alpha^{1/3}}\right) \, , \tag{21}$

where  $\text{Ai}(x)$  is the standard Airy function. The boundary condition, eq. (17), in this case leads to  $\frac{1}{4}\xi_0^2 = \alpha + (-\text{ai}_0)(\alpha)^{1/3}$ , where  $\text{ai}_0$  (negative) is the first zero of the Airy function, corresponding to the highest negative energy eigenvalue. The appropriate conversion into the  $\epsilon_N(a)$  dependence now yields

$\epsilon_N(a) \approx -\theta(a) [1 + \tfrac{1}{2}(\kappa a)^2] \approx -\theta(a) \cosh(\kappa a) \, ,$ 
$$\text{when} \quad \xi_0 \gg 1 \, . \tag{22}$$

After obtaining solutions of the boundary condition in both limiting cases we can now investigate the form of the polyelectrolyte distribution between the two surfaces, fig. 3. In the limit  $\xi_0 \gg 1$  we clearly observe that polymer segments are mostly distributed close to the boundary surfaces with negative  $\epsilon_N(a)$ , leaving a small depleted region right at the surfaces and a larger one close to the middle of the intersurface space. This signifies that the polyelectrolyte chain is surface bound in this limiting case [6]. This soft adsorption of the polyelectrolyte chain is being promoted by the attractive electrostatic interactions between the polyelectrolyte and the oppositely charged surface-bound charges. The effect of the polymer steric confinement is meagre in this case.

In the opposite extreme  $\xi_0 \ll 1$  the electrostatic effects are only a first order perturbation to the purely

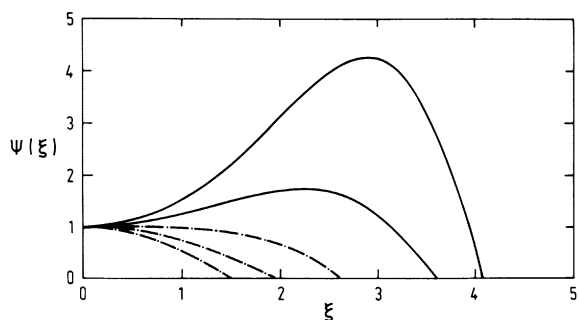


Fig. 3. Behavior of the unnormalized solution, eq. (16) (square root of the local polyelectrolyte segment density) for different values of  $\alpha$ . The bold lines correspond to  $\alpha > 0$  and the semi-dashed lines to  $\alpha \leq 0$ .  $\alpha$  goes from +2 (top curve) to -2 (bottom curve) in steps of one. Clearly for  $\alpha > 0$  there is a more or less pronounced crowding of the polymeric chain close to the surfaces where  $\psi(\xi) = 0$ . In the opposite case the chain is mostly distributed around the middle of the intersurface space ( $\xi = 0$ ). These two distinct cases of polyelectrolyte density profile correspond to surface-bound and extended configurations.

steric interactions. The polymer segment density, fig. 3, behaves as if the charges would be absent and we have a depleted region close to the surfaces with most of the chain concentrated at the middle of the intersurface space. The polyelectrolyte chain is not surface bound in this case since the electrostatic attraction is not large enough to overcome the steric confinement forces. In the limit of  $a \rightarrow 0$  the steric confinement forces would therefore always prevail irrespective of the amount of charge on the surfaces.

## 5. Discussion

Let us review briefly all the approximations interspersed along the way to an approximate analytical solution of section 4. There is first of all the saddle-point approximation, corresponding to the mean-field (Poisson-Boltzmann) solution for the electrostatic potential. This approximation scheme will work as long as the correlation effects are small (overall small charges). We can nevertheless expect it to be a first-order term in a hierarchy of approximations taking into account the deviations from the most probable thermodynamic configuration. The ground-state dominance ansatz should not be viewed as a

real approximation, since we want to deal with a thermodynamic limit where all finite size effects are of no importance. Furthermore the limit of  $\kappa a \ll 1$  was introduced with the sole purpose of not getting entangled into a web of mathematical technicalities connected with the solutions of the modified Mathieu equation. The complete solution valid for any  $\kappa a$  will be found in an enlarged version of this short report [10].

Finally we remain with the Wiegell approximation, the only approximation that sets some serious limits on our results. It states that the direct interactions of the charges on the polymer beads with the surfaces should be larger than the interaction between polyelectrolyte charges themselves. Such a regime always exists for a polyelectrolyte immersed in a salt solution for sufficiently small  $\tau$ . However, if our model system would be composed of a single polyelectrolyte chain, with no added salt, throwing away the first term in eq. (10) would mean throwing away the whole thing. For this particular system the Wiegell approximation would never be valid and the solution of SC-PBP equations would have to be sought along a different route [17].

Let us now review the behavior of  $\epsilon_N(a)$ , fig. 4, for different values of  $\xi_0$ , which for constant  $\tau$  still depends on the surface charge density and surface separation, eq. (17). Let us start by considering the limit of  $\sigma \rightarrow 0$ . In this case the dominant contribution to the chain free energy (the first term in eq. (18)) is just the steric confinement term, eq. (20), and  $\epsilon_N(a)$  remains positive for all values of  $a$ . The conformation of the polyelectrolyte chain in this limit is always unbound with a majority of the beads concentrated near the middle of the intersurface space, leaving behind depleted regions close to the bounding surfaces.

At a finite but still small  $\sigma$ , the  $\epsilon_N(a)$  curve will develop a local minimum at a finite value of  $a$ , approaching the asymptotic form  $\epsilon_N(a) \approx (\pi/2)^2 (\kappa a)^{-2}$  for small values of  $a$ . This follows simply by inspecting the behavior of  $\theta(a)$ , eq. (13). Finally as  $\sigma$  becomes large we are in the regime described by eq. (22) except for very small values of  $a$ , when the steric confinement overwhelms any electrostatic contribution to  $\epsilon_N$ . For almost all values of  $a$  the chain free energy is therefore negative and the polyelectrolyte chain is in a surface-bound state, with a very

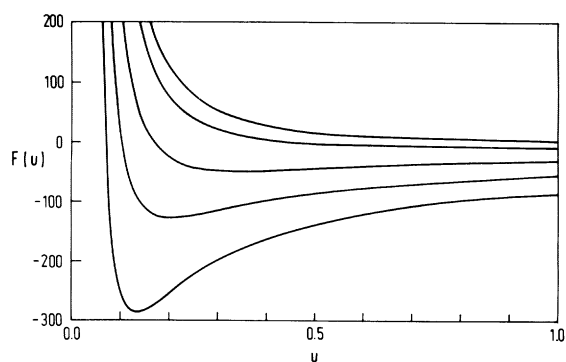


Fig. 4.  $F(u) = \epsilon_N$  as a function of dimensionless separation  $u = \kappa a$ , obtained from numerical solution of the boundary condition, eq. (17), fig. 2, for different values of surface charge density expressed through a dimensionless constant  $h_0^2 = 6\beta\tau\sigma/\epsilon\epsilon_0\kappa(\kappa l)^2$ . The uppermost curve corresponds to an uncharged polymer ( $h_0 = 0$ ) with pure steric exclusion at the surfaces. The other curves correspond to  $h_0 = 10, 30, 50, 75$  (the lowest curve is for  $h_0 = 75$ ). Beyond the local minimum the energy curves correspond to an attractive contribution to the total force between the charged surfaces ( $d\epsilon_N(a)/da < 0$ ). For large enough  $h_0$ , moving from large to small separations ( $u$ ) there is a transition from surface bound ( $\epsilon_N < 0$ ) to extended conformation ( $\epsilon_N > 0$ ) of the confined polyelectrolyte chain.

small depletion layer right at the surfaces. Most of the chain is concentrated close to the surfaces leaving another depleted region around the middle of the intersurface space. For large enough  $\sigma$  as we go from large to small intersurface separation the originally surface-bound chain, can desorb on approach of the surfaces. The details of this process can be adequately described only after a careful investigation of the limit  $a \rightarrow \infty$  [10].

The most important characteristics of the free energy curve  $\epsilon_N(a)$ , fig. 4, are regions of attractive interactions ( $d\epsilon_N(a)/da < 0$ ) that set in for sufficiently large surface charge density in addition to the standard (PB) repulsive forces (the second term in eq. (18)). The same phenomenon has been observed in the case of no added salt [4] where it was shown to stem from the bridging of polyelectrolyte chains from one surface to the other one. This remains true for our system and is especially clear in the case of surface bound states ( $\epsilon_N(a) < 0$ ), where the polyelectrolyte chain is mostly trapped in the vicinity of the surfaces. Regions of the chain that are not trapped and extend from one surface to the other one acts as "elastic springs", softly (electrostatically)

bound with their ends to the surfaces, that tend to draw the surface together. The bridging contribution to the polyelectrolyte free energy is therefore mostly elastic in origin.

Forces between charged surfaces are apparently much more complicated if the intervening medium contains a polyelectrolyte chain. The attractive interaction that sets in for some particular values of the system's parameters is a consequence of bridging of the polyelectrolyte chain between two partially collapsed states close to the surfaces. The fact that this attraction can be described already in the frame of a mean-field theory sets the whole problem quite apart from the standard PB theory, where attraction comes in only in the regime where the mean-field description breaks down.

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